

RESEARCH ACTIVITIES ON MARINE METHANE HYDRATES AND CO₂ SEQUESTRATION

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Abstract— CO₂ and methane hydrates in the deep ocean are being investigated as part of joint R&D programs between the University of Hawaii and the U.S. Naval Research Laboratory. CO₂ hydrates are being studied to support research on ocean sequestration of CO₂ as a means to reduce greenhouse gas emissions into the atmosphere. The primary objectives of the methane hydrates R&D program are to determine the distribution and availability of the marine methane hydrates resource; to develop viable detection, recovery, and applications technologies; and to evaluate the impact of methane hydrates on the local marine environment and their role in the global carbon cycle. The joint programs involve both field and laboratory studies. This paper provides a brief overview of the ongoing research.

1. BACKGROUND

Hydrates are crystalline solids comprising water molecules linked by hydrogen bonds in a tight polyhedral cage structure. Guest molecules, which can include CO₂ or various hydrocarbons found in natural gas mixtures, reside in the interstices of this lattice. Both CO₂ and hydrocarbon hydrates occur naturally in the deep ocean (Sakai *et al.*, 1990; Kvenvolden *et al.*, 1993).

CO₂ hydrates have been the focus of interest over the past decade in relation to ocean sequestration of CO₂. Increasing atmospheric levels of CO₂ and other greenhouse gases have the potential to alter global climate. Studies and policies are being pursued to reduce anthropogenic greenhouse gas emissions. One technique that is being assessed involves extraction of CO₂ from combustor flue gases, followed by liquefaction and sequestration in the deep ocean. If CO₂ is injected directly into the ocean at a depth greater than about 400 m, then CO₂ hydrates can form. This solid hydrate phase will impact dissolution and dispersion of the CO₂ and can pose an operational problem due to blockage of injectors and internal passages in the CO₂ conveyance system. The stability of the hydrate can influence the period of time that the CO₂ remains trapped in the ocean and, hence, the effectiveness of this greenhouse gas sequestration strategy.

Natural gas hydrates (hereinafter referred to interchangeably as methane hydrates—since methane is the most abundant hydrate-forming component of natural gas) represent an enormous untapped hydrocarbon resource. Estimates of the total volume of hydrocarbons locked in hydrate deposits worldwide range widely from about 10⁵ trillion standard cubic feet (TCF) to 2.7 x 10⁸ TCF (i.e., 2.8 x 10¹⁵ to 7.6 x 10¹⁷ cubic meters). Even at the lower end of this range, this

resource could potentially satisfy the energy needs of the world for centuries, provided that practicable recovery techniques can be devised.

While offering tremendous opportunities as a future primary energy resource, marine hydrate deposits also represent an immediate and formidable nuisance to offshore oil and gas operations (Max & Cruickshank, 1999; Cruickshank & Masutani, 1999). This problem has become more critical as these commercial activities move into increasingly deeper waters. From a defense perspective, there is a need to characterize the geoacoustic properties of hydrate sediments and to assess their potential as an *in situ* offshore energy source, since this information is relevant to Naval operations. Finally, methane hydrates may exercise a profound effect on global climate if carbon sequestered in these solids is released into the environment by commercial exploitation of the fuel or through destabilization and outgassing induced by ocean warming (MacDonald, 1990).

The promise and peril associated with methane hydrates has led to recent national RD&D programs in Japan, India, and the U.S. Research funding for marine methane hydrates has also increased in a number of European Union and Asian nations, with significant growth anticipated in the near term.

The University of Hawaii (UH) and the U.S. Naval Research Laboratory (NRL) have been collaborating on two joint research programs that investigate hydrates in the deep ocean. CO₂ hydrates are being studied as part of an international field experiment in which about 40 tonnes of liquid CO₂ will be injected through an array of nozzles at an open ocean site at a depth of about 800 m. Methane hydrates studies include laboratory and field investigations to determine the distribution and availability of this resource; to develop viable detection, recovery, and applications technologies; and to evaluate the impact of methane hydrates on the local marine environment and their role in the global carbon cycle. This paper provides an overview of the primary joint research activities.

2. CO₂ HYDRATES

Research on CO₂ hydrates at UH and NRL currently is being conducted in support of two projects. UH and NRL are participants in an international field experiment on CO₂ ocean sequestration (Masutani & Takahashi, 2000; Herzog *et al.*, 2001). For this project, laboratory investigations of CO₂ hydrate behavior have focused on issues related to pipeline and injector blockage phenomena and the impact of hydrate formation on CO₂ droplet dissolution. UH also is studying CO₂ hydrates as part of a project funded by the U.S. Department of Energy to explore the technical feasibility of CO₂ sequestration in the negative buoyancy regime, below about 3,000 m depth in the ocean. Liquid CO₂ discharged at these depths will sink and could pool on the sea floor. Hydrates may impede dissolution of the CO₂ into the sea water, which some proponents contend could increase the term of sequestration and reduce local environmental impacts.

2.1 International Field Experiment

The international field experiment on CO₂ ocean sequestration is an R&D collaboration between the Governments of Japan, the United States, Norway, Canada, and Australia to develop

technology solutions to reduce greenhouse gas emissions. The experiment is being implemented by an team of scientists and engineers from the participating countries. Support also is being provided by two private sector entities, Asea Brown Boveri (ABB) and the Central Research Institute of the Electric Power Industry of Japan. The experiment plans to inject pure liquid CO₂ at various flow rates at a depth of about 800 m in the ocean and to monitor the effects of this injection with mobile and moored instruments. Data obtained in the tests will be applied to develop models to evaluate the environmental impacts of ocean sequestration. The specific objectives of the field experiment are:

1. investigate CO₂ droplet plume dynamics through qualitative flow visualization (using mobile video cameras) and quantitative measurements of velocity and pH in the plume and on its margins;
2. clarify the effects of hydrates on droplet dissolution through visualization of the droplet phase and measurements of the vertical extent of droplet rise using scalar indicators (either pH or other added tracers);
3. trace the evolution of CO₂-enriched sea water that peels from the plume by performing a three-dimensional mapping of the velocity and relevant scalar (e.g., pH or DIC) fields; and
4. assess potential impacts on marine biota by quantifying variations in bacterial biomass, production, and growth efficiency associated with induced changes in seawater pH, and through observations of the vitality and mortality of higher organisms in the sediment and water column.

In support of the field experiment, laboratory investigations are being conducted to address concerns related to hydrate blockage of injectors and pipelines. Tests are being performed by the international team in pressure facilities at UH and the Southwest Research Institute. Figure 1 presents some representative video frames obtained in a series of experiments to assess the risk of hydrate blockage in a prototype multi-orifice injector.

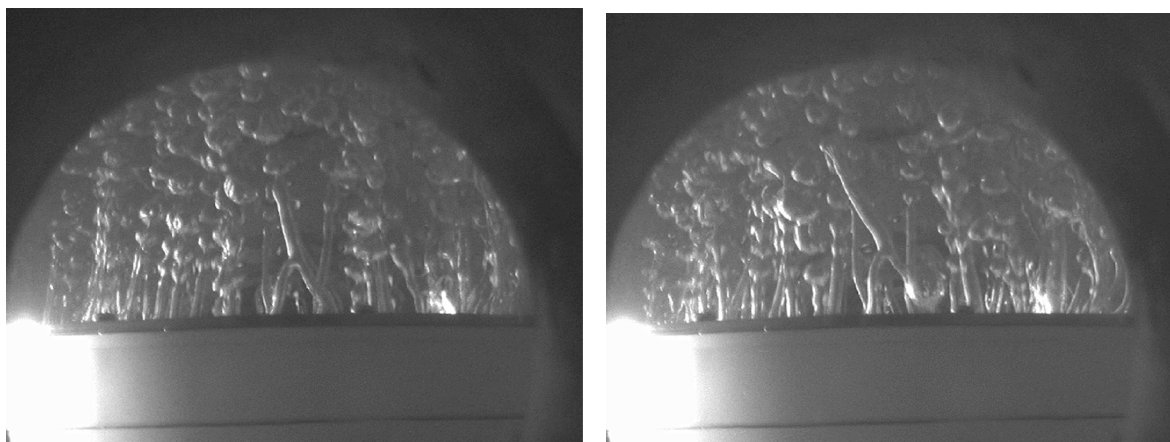


Figure 1 Hydrate tubes formed at the CO₂ injector under simulated deep ocean conditions.

2.2 Laboratory and Modeling Studies of Deep Ocean Sequestration

The deployment and operation of disposal conduits to depths of 3,000 m or more has not been demonstrated. Provided that this technical uncertainty can be addressed, sequestration of CO₂ in the negative buoyancy regime presents a number of advantages. The results of modeling studies indicate that the term of sequestration increases with depth (Nihous *et al.*, 1994; Nihous *et al.*, 1996; Orr *et al.*, 2001). Furthermore, it has been contended that environmental impacts associated with a pool of discharged liquid CO₂ and hydrates on the sea floor may be less severe than those associated with dissolution and dispersion at intermediate depths. This point is a topic of debate.

Field and laboratory studies suggest that phenomena associated with deep CO₂ discharges at depths of 3,000 m or more will not differ significantly from behavior observed at shallower depths. The propensity to form solid hydrates, however, is expected to increase modestly with depth. This may pose an elevated risk of blockages in the injector and pipeline and could impact injector performance if hydrate formation proceeds rapidly enough to affect the fluid instability that leads to break up of the CO₂ discharge jet into a dispersed droplet phase.

The U.S. Department of Energy is supporting a study led by McDermott Technology, Inc. to investigate the technical and economic feasibility of large-scale CO₂ transportation and sequestration at depths of 3,000 m or greater. UH is a partner in this study and is developing models of sinking plumes of CO₂ droplets and hydrates; and conducting laboratory experiments to elucidate CO₂ hydrate blockage phenomena and to clarify the influence of hydrate formation on the break-up of liquid CO₂ jets into a dispersed phase. The hydrate blockage tests are being conducted in parallel with the blockage experiments being pursued in support of the international field experiment.

Hydrate formation can effect the characteristics of the discharged CO₂ phase. Liquid CO₂ injected into sea water is hydrodynamically unstable and will break up into droplets. The size spectra (distribution) of this droplet phase will impact the dissolution and dispersion of the CO₂. The surface hydrodynamic instability that causes the break-up of the CO₂ effluent can be affected by the formation of solid hydrates at the interface between the water and the CO₂. This may lead to changes in the size spectra.

Adopting the approach proposed by Teng *et al.* (1996), it has been assumed that the effect of hydrate formation on jet break up can be assessed by comparing their respective characteristic time scales, t_f and t_b . When jet break up time is comparable to or much shorter than the characteristic time for hydrate formation, i.e., when $t_b \approx t_f$ or $t_b \ll t_f$, jet break up will be determined purely by hydrodynamics and is unaffected by hydrate kinetics. When $t_b \gg t_f$, a thin hydrate layer forms on the jet surface at the early stage of instability. Since this layer separates the CO₂ and seawater phases, surface deformation of the jet is impeded and, thus, the jet remains stable. This can give rise to the formation of hydrate ‘tubes’ that have been observed at CO₂ seeps in the ocean (Sakai *et al.*, 1990).

Experiments are underway that examine a range of relative values of t_f and t_b . Digital video flow visualization records and Phase Doppler Particle Analyzer droplet size data are being analyzed to identify changes induced by varying the characteristic times.

To complement the laboratory studies, models have been developed to clarify the relationship between the conditions of discharge (i.e., size of CO₂ droplets and solid hydrate particles produced by the injector; initial fraction of CO₂ converted to hydrates; distance above the sea floor; flow rate; etc.) and the dissolution and dispersion of the effluent in the region adjacent to the injection point. As a starting point, a simple one-dimensional analysis of a sinking plume was conducted. Details of this model are provided in Masutani (2001). Figure 2 presents model predictions of sea water pH for different CO₂ deep injection scenarios (i.e., 100 kg/s of CO₂ discharged at 3,000 m as 5, 10, and 20 mm diameter droplets with hydrate films). The two dimensional pH field was inferred from the one dimensional model results by assuming an axisymmetric Gaussian plume.

3. METHANE HYDRATES

Methane (natural gas) hydrates are the subject of the second collaborative R&D program between UH and NRL on marine hydrates. This program involves both field and laboratory studies and has a strong international component. As mentioned above, the primary objectives of the program are to determine the distribution and availability of the marine methane hydrates resource; to develop viable detection, recovery, and applications technologies; and to evaluate the impact of methane hydrates on the local marine environment and their role in the global carbon cycle.

3.1 Field Studies

NRL is the technical lead for field studies to characterize the properties of marine methane hydrates from different regions and to assess the distribution of the resource. Research cruises and hydrate sample collection have been undertaken in the Gulf of Mexico (Texas-Louisiana shelf), Norwegian-Greenland Sea, and the Cascadia Margin (Coffin *et al.*, 1999). Figure 3 shows a surface outcropping of methane hydrates encountered in the Gulf of Mexico. Hydrate samples collected during recent research cruises have been analyzed by Japanese researchers at AIST Hokkaido as part of an international partnership.

The development of field instrumentation to detect hydrates in sediments and methane seeps is a major thrust of the R&D program. In particular, DTAGS (Deep Towed Acoustics/Geophysics System) offers tremendous potential for hydrate resource exploration. DTAGS is a multichannel seismic system that is towed from a ship to obtain high resolution seismic data sampling of the ocean bottom and sub-bottom. Spatial resolution of about 5 m vertical and 15 m horizontal are possible in the upper 1 km of the sediment. DTAGS has been used successfully in surveys of hydrate fields in the Blake Ridge and Nankai Trough. Additional information on DTAGS is available online at <http://www.nrlssc.navy.mil/~hydrates/dtags.htm>.

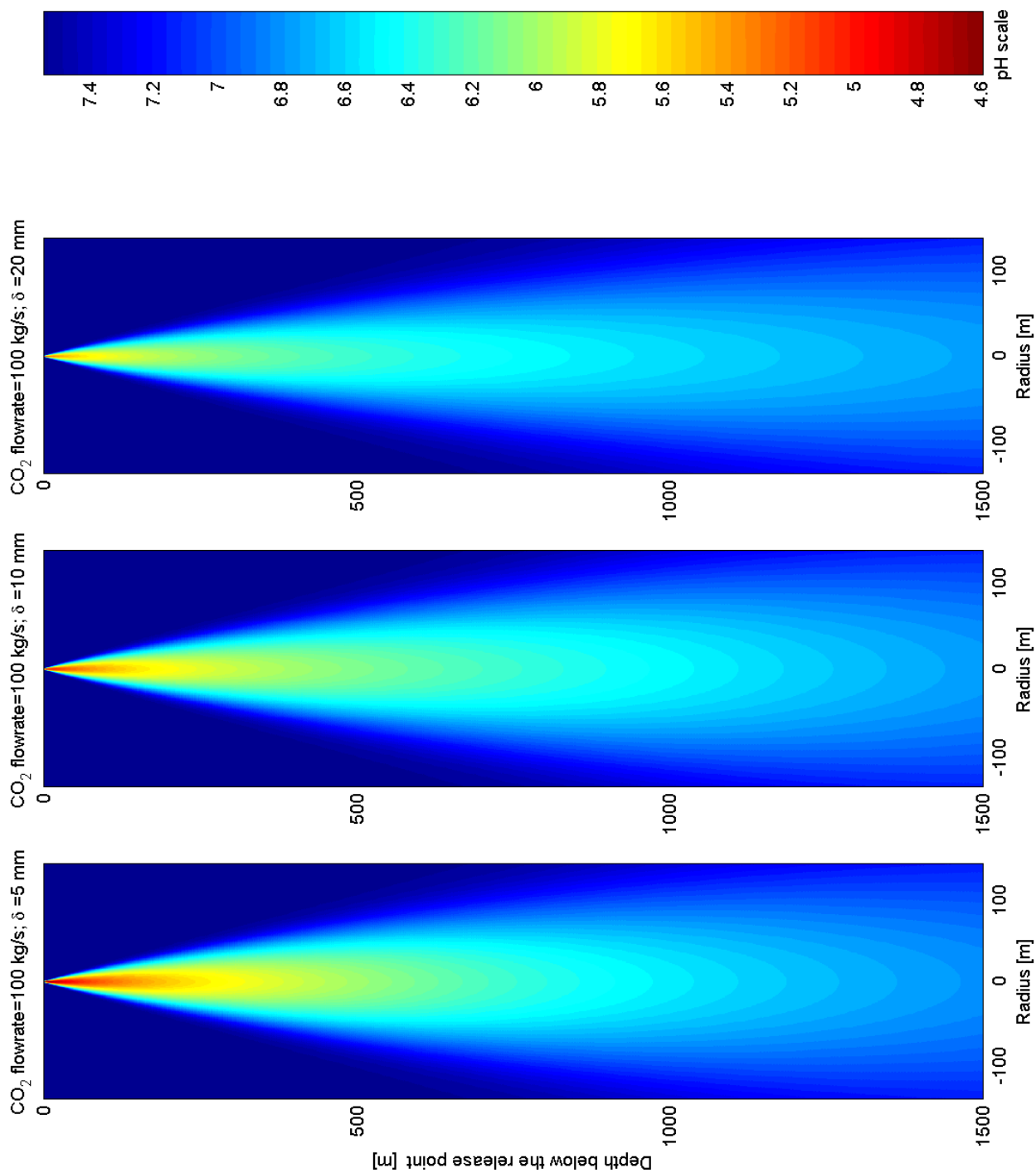


Figure 2 Predicted pH fields adjacent to the CO_2 discharge point at 3,000 m depth.



Figure 3 Methane hydrates (yellow color) on the sea floor in the Gulf of Mexico.

3.2 Laboratory Studies

Fundamental laboratory studies of hydrate kinetics and stability are being conducted at UH and NRL. Funding was recently received from the Office of Naval Research for these activities and test facilities are being expanded. Experiments are being conducted in a number of fully-instrumented pressure chambers, with internal volumes ranging from several liters to 700 liters, that can simulate conditions in the ocean down to about 1,000 m depth. Diagnostics include Raman spectroscopy, X-ray diffraction, mass spectrometry, and digital video imaging. Figure 4 provides a photograph of one of the pressure chambers being used in several studies, including the development of a benthic fuel cell. This chamber contains a layer of sea floor sediment beneath a column of pressurized sea water.



Figure 4 Pressure chamber for hydrates studies.

3.3 Benthic Fuel Cells

While large scale, commercial recovery of marine methane hydrates for onshore energy production is unlikely to occur in the immediate future, certain specialized applications may be practicable in the near term. Specifically, there is a need for low level, long term power sources for instruments deployed on the sea floor. In areas with natural gas hydrates or seeps, these hydrocarbons could serve as an *in situ* energy source. Toward this end, NRL and UH are actively pursuing development of benthic batteries and methane hydrate fuel cells in cooperation with several industrial and university partners.

The principal tasks at this time are to demonstrate the feasibility of technologies to extract dissolved oxygen from sea water in sufficient quantity to sustain fuel cell operation; and to develop practicable approaches to destabilize methane hydrates and collect the released methane. Several fuel cell types are under consideration and will be tested in the field and in the laboratory under simulated deep ocean conditions.

3.4 International Program

A cornerstone of the collaborative program between UH and NRL is the establishment of an international research partnership that will share resources and information to advance methane hydrate science and technology. The rationale for such a partnership is that methane hydrates represent a huge resource that has the potential to restructure the world energy economy. Furthermore, global climate may be affected as carbon sequestered in these hydrates is released into the environment as a result of future resource exploitation or inadvertently through destabilization and outgassing induced by ocean warming. The international community will share the associated burdens and benefits. This common interest supports an international approach to address key research issues.

As part of the present program, several joint research proposals with scientists from Japan, Korea, and Norway have been prepared and are under review. These joint projects include field studies, laboratory experiments, and the creation and management of databases. In addition, UH and NRL, in cooperation with AIST Hokkaido, Inha University of Korea, and the Pacific International Center for High Technology Research, organized a international expert workshop on methane hydrates in March 2001. The workshop objectives were: (1) to review past, ongoing, and planned methane hydrates R&D projects and programs; (2) to share information on budgets and research resources and priorities in different countries; and (3) to establish linkages for domestic and international partnering. Funding for the workshop was provided by UH and through grants from the Office of Naval Research-International Field Office and the United States Department of Energy. Fifty eight participants from the U.S., Japan, Korea, Canada, Norway, Russia, and the U.K. attended the workshop. A meeting report will be released by the end of 2001.

4. SUMMARY

CO₂ and methane hydrates in the deep ocean are being investigated as part of joint R&D programs between the University of Hawaii and the U.S. Naval Research Laboratory. CO₂ hydrates are being studied to support research on ocean sequestration of CO₂ as a means to reduce greenhouse gas emissions into the atmosphere. Field, laboratory, and modeling activities are being pursued to investigate hydrate blockage phenomena, to clarify the influence of hydrate formation on the break-up of liquid CO₂ jets into a dispersed phase, and to elucidate the relationship between the conditions of CO₂ discharge (i.e., size of CO₂ droplets and solid hydrate particles produced by the injector; initial fraction of CO₂ converted to hydrates; distance above the sea floor; flow rate; etc.) and the dissolution and dispersion of the effluent in the region adjacent to the injection point.

The methane hydrates research program involves both field and laboratory studies and has a strong international component. The primary objectives of the program are to determine the distribution and availability of the marine methane hydrates resource; to develop viable detection, recovery, and applications technologies; and to evaluate the impact of methane hydrates on the local marine environment and their role in the global carbon cycle. Scientists and engineers from government agencies, universities, and the private sectors in the U.S., Korea, Japan, and Norway have agreed to collaborate in the investigations.

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